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D.C. Bias Effect on the Dielectric Behaviour of Some Disperse Systems (Commemoration Issue Dedicated to Professor Tetsuya HANAI On the Occasion of His Retirement)

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D.C. Bias Effect on the Dielectric Behaviour of Some Disperse Systems

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Dielectric measurements were carried out for some heterogeneous systems such as various kinds of planar membrans in an aqueous phase and suspensions under application of d.c. bias voltage. Frequency dependence of the capacitance and the conductance, the so-called dielectric relaxation, was observed for most of the systems adopted in the experiments. The system of cation-exchange membranes CMV immersed in distilled water showed a couple of dielectric relaxations attributed to their heterogeneous structure. A dielectric theory developed for the system containing a concentration polarization layer caused by the application of d.c. bias voltage was applied to the observations. The structural parameters such as the thickness and the conductivity gradient of the concentration polarization layer, the capacitances and the conductances of the two adjoining aqueous phases were calculated from the dielectric parameters characterizing a double relaxation pattern observed. The theoretical analysis interpreted the double dielectric relaxations very satisfactorily.

KEY WORDS: Dielectric relaxation/ Disperse system/ Cation-exchange membrane/ Concentration polarization/ Bias voltage

1. INTRODUCTION

It is known that heterogeneous systems composed of some distinct phases show dielectric relaxations due to interfacial polarization. Such kinds of heterogeneous systems are readily found as a number of examples: polymer film-aqueous solution systems, emulsions, suspensions, lipid vesicles, microcapsules, biological suspensions, and the like.¹⁻⁷⁾

Theoretical analysis for the respective dielectric relaxations succeeded in estimating several parameters characterizing the respective heterogeneous structure: permittivities and conductivities of the constituent phases, thickness for the lamellar structure and volume fractions of the constituent phases.

Following the conventional dielectric measurement, these investigations were all carried out under no d.c. bias voltage over the specimens. It is, however, expected that application of d.c. bias voltage to the specimens gives rise to something change in structure of these heterogeneous systems.

In the present study, an attempt is made to carry out dielectric observation, under application of d.c. bias voltage, of various kinds of heterogeneous systems: ion-exchange membrane, dialysis membrane, reverse osmosis membrane, filtration membrane, O/W emulsion and polystyrene latex. As a result of the d.c. bias application, most of the heterogeneous systems showed a remarkable change in the dielectric

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relaxation patterns.

Further, a dielectric analysis based on a dielectric theory of concentration polarization layer caused by the application of d.c. bias voltage was carried out on the system of the cation-exchange membrane CMV in distilled water to estimate the structural parameters of the heterogeneous system such as the thickness of the concentration polarization layer and the local gradient of the conductivity.

2. EXPERIMENTAL

2.1 Materials

2.1.1 Ion-Exchange membrane

Ion exchange membranes adopted were cation exchange membranes Selemion CMV and anion exchange membranes Selemion AMV supplied by Asahi Glass Co. Ltd. Japan. The fixed charge density of the membranes is about 1 mequiv/cm³, the water content being about 30 wt.%. The membranes were immersed in a 3M NaCl solution to adjust the ionic form. Next, the membranes were rinsed in distilled water.

2.1.2 Dialysis Membrane

The dialysis membrane used in this work was the product by Visking Co. Ltd. U. S.A. D.c. voltage 100 V was applied to the system of the membrane and distilled water for 60 min. for washing out foreign materials adsorbed on the surface prior to dielectric measurements.

2.1.3 Reverse Osmosis Membrane

The reverse osmosis membrane used in this work was DRS10, which was kindly supplied by Daicel Co. Ltd. Japan. The degree of rejection of salts (DRS) on the membrane is 10%. Thickness of the membrane was estimated to be 70 μ m by measuring with a micrometer.

2.1.4 Some Filtration Membranes

1) *Sartorius Membranfilter* The membranes are made of cellulose acetate and have number of pores with 0.1 μ m in diameter. The thickness of the membranefilters was 80 μ m. In order to prevent air from remaining in the pores, the membranefilters were immersed in ethyl alcohol for 40 min., then being rinsed in distilled water repeatedly before use.

2) *Nuclepore membrane* The membranes with very uniform and perfectly round and cylindrical pores are made of polycarbonate and are hydrophilic in nature. The diameter of pores of the membranes was 0.1 μ m.

3) *Milliporefilter* The millipore filters used in this work were made of the mixture of cellulose acetate and cellulose nitrate. Pore size of the filters was 0.2 μ m in diameter. In order to remove air from the pores, an alcohol pretreatment for the filters similar to Sartorius membrane was carried out before use.

2.1.5 Oil-in-Water Emulsion

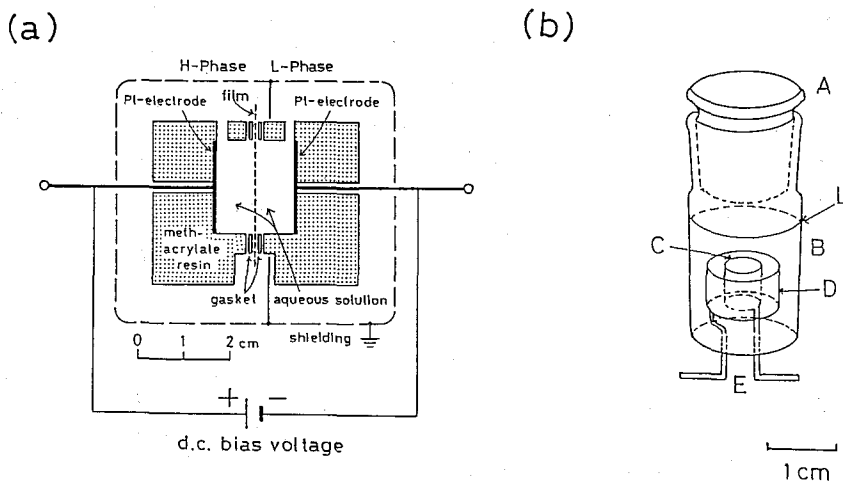


Fig. 1. (a) A cell system for measuring a.c. impedance of a solution/film/solution system under application of d.c. bias voltage; (b) A measuring cell for dielectric measurements of emulsions and polystyrene latex. (A: Glass stopper, B: Glass Vessel, C: Inner Electrode(Pt), D: Outer Electrode(Pt), E: Lead Wires(Pt), L: Level of specimens.)

Non-ionic surfactant Tween 20 (polyoxyethylene sorbitan monolaurate) was adopted as an emulsifier. The oil phase for the O/W emulsion was a mixture of kerosene and carbon tetrachloride (3:1 by volume), and contained Tween 20 (4% by volume). The oil phase prepared was added to distilled water. Stable O/W emulsions were readily obtained by shaking the mixture.

2.1.6 Polystyrene Latex

Polystyrene latex composed of polystyrene granules with 177 nm in diameter was employed in this work.

2.2 Dielectric Measurement

Two kinds of measuring cells were employed in this work: one is for membrane systems and the other for spherical disperse systems. Figure 1(a) shows a measuring cell system for membrane immersed in distilled water. The cell made of methacrylate cylindrical compartments between the electrodes were separated by the specimen film. The area of the electrode was 3.14 cm^2 and the distance between the two electrodes was 1.4 cm. The cell was constructed in such a way that the effective area of the electrodes was equal to those of the specimen film and the cross section of the compartments. Both the compartments were filled with the same aqueous solution, that is distilled water in this experiments. The measuring cell for polystyrene latex and emulsion consisted of two concentric platinum cylinders as shown in Fig. 1(b).

The dielectric measurements were carried out with Yokogawa Hewlett Packard 4192A LF Impedance Analyzer operating in a range of 5Hz–13MHz. A.C. 1V rms was applied to the measuring cell for a.c. impedance measurement. Application of d.c. bias voltage to the cell systems was conducted with a self-sustained function of the

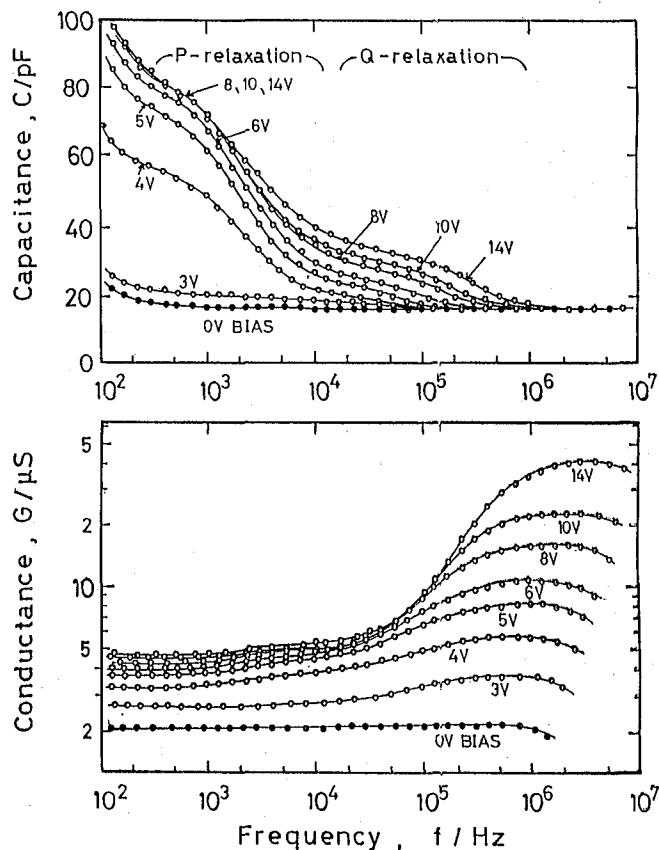


Fig. 2. Frequency dependence of capacitance C and conductance G for the whole system composed of a cation exchange membrane CMV and distilled water under application of d.c. bias voltages (0V to 14V)

analyzer.

In order to equilibrate the membranes with the aqueous phase, all the membranes were kept in distilled water overnight before dielectric measurements. The measurements were carried out at 25°C.

3. RESULTS AND DISCUSSION

3.1 Dielectric Behaviour of Systems in Planar Structure

3.1.1 Ion-exchange Membrane

Figure 2 shows the results of dielectric measurement for the cation-exchange membrane CMV in distilled water. No dependence of the capacitances and the conductances on the measuring frequencies was found at all under bias voltage 0V, being considered to be due to the very conductive CMV membrane.

On application of d.c. bias voltages, the capacitances and the conductances of the system showed remarkable dependence on measuring frequencies. A couple of dielectric relaxations was found for respective values of d.c. bias voltage in the figure.

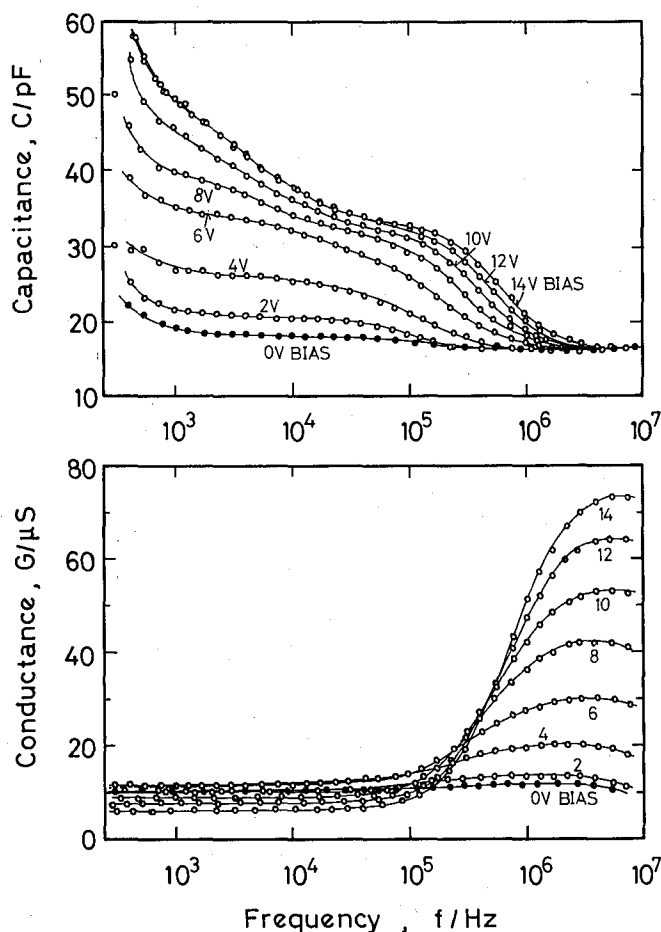


Fig. 3. Frequency dependence of capacitance C and conductance G for the whole system composed of an anion exchange membrane AMV and distilled water under application of d.c. bias voltages (0V to 14V)

The relaxations at a lower frequency side are termed P-relaxation and those at a higher frequency side Q-relaxation. A double dielectric relaxation of this kind was observed markedly under d.c. bias voltage more than 4V. The P-relaxation is almost unchanged with the bias voltage more than 8V, whereas the Q-relaxation increases in magnitude and shifts to higher side of frequencies with increasing d.c. bias voltage. A steep rise in the capacitance at frequencies lower than 200 Hz is attributed to electrode polarization, which is out of the present discussion.

The double dielectric relaxations observed may be caused by interfacial polarization among a concentration polarization boundary layer and two distinct aqueous phases located on both sides of the boundary layer. A detailed analysis of the dielectric data and discussion of the structure of concentration polarization boundary layer were already reported in previous papers.⁸⁻⁹⁾

A similar results were also obtained on the system of AMV membrane immersed in distilled water, being shown in Fig. 3. The P-relaxations for AMV membrane are

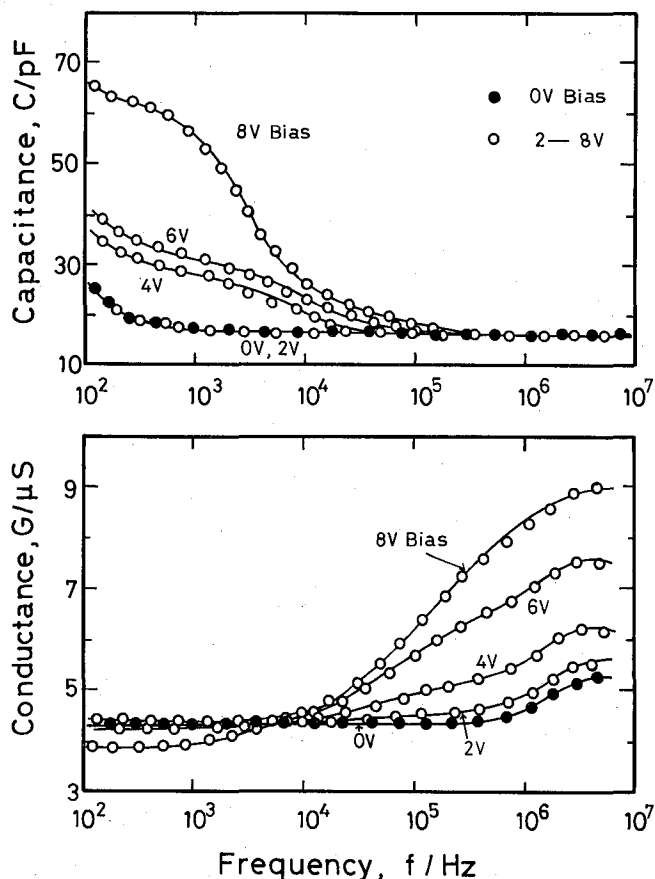


Fig. 4. Frequency dependence of capacitance C and conductance G for the whole system composed of a Visking dialysis membrane and distilled water under application of d.c. bias voltages (0v to 8v).

smaller as compared with those for CMV membrane.

3.1.2 Visking Dialysis Membrane

In contrast with the fixed-charge membranes CMV and AMV, Visking dialysis membrane was adopted as an example of non-charged membrane. Figure 4 shows the results of dielectric measurements on the system composed of Visking dialysis membrane and distilled water. A marked dielectric relaxation was observed on application of d.c. bias voltages more than 4V. The relaxation profile is characterized by the double relaxation similar to the case for ion-exchange membrane systems. The Q-relaxation for the Visking membrane system is rather small and shifts to lower frequencies in comparison with the case for the CMV membrane system.

3.1.3 Reverse Osmosis Membrane

Another example of non-charged membranes is reverse osmosis membranes. Dielectric relaxations under application of no d.c. bias voltage for reverse osmosis

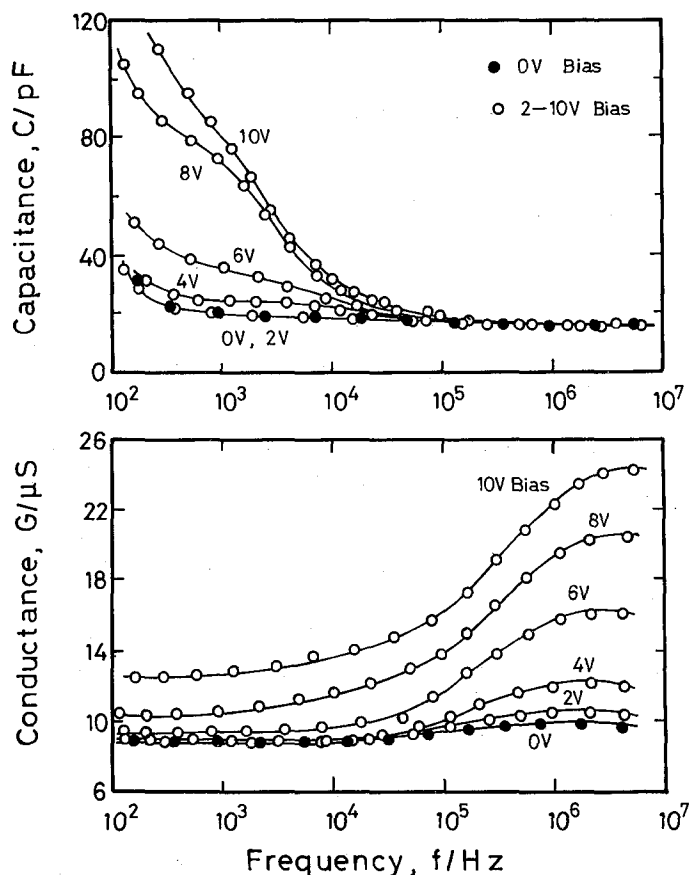


Fig. 5. Frequency dependence of capacitance C and conductance G for the whole system composed of a reverse osmosis membrane DRS10 and distilled water under application of d.c. bias voltages (0V to 10V)

membranes DRS97 immersed in salt solutions were observed by Asaka¹⁰, who attributed the relaxation to low conductivity of membrane DRS97. In contrast with the DRS97, the present membrane DRS10 showed no dielectric relaxation probably owing to rather high conductivity of DRS10.

In the present study, the membrane DRS10 was adopted to examine the effect of d.c. bias voltage. The results were shown in Fig. 5. It is readily seen in Fig. 5 that marked frequency dependence of the capacitance C and the conductance G was observed under application of d.c. bias voltage. The results suggest that a concentration polarization boundary layer is generated alongside the membrane on application of d.c. bias voltage.

3.1.4 Some Filtration Membrane

Figures 6, 7 and 8 show frequency dependence of the capacitance C and conductance G observed for Sartorius membranfilter, Nuclepore membrane and Milliporefilter. A marked bias effect was also observed for each membrane. The dielectric relaxation patterns observed for these membranes shown in Figs. 6, 7 and 8 are similar to that of

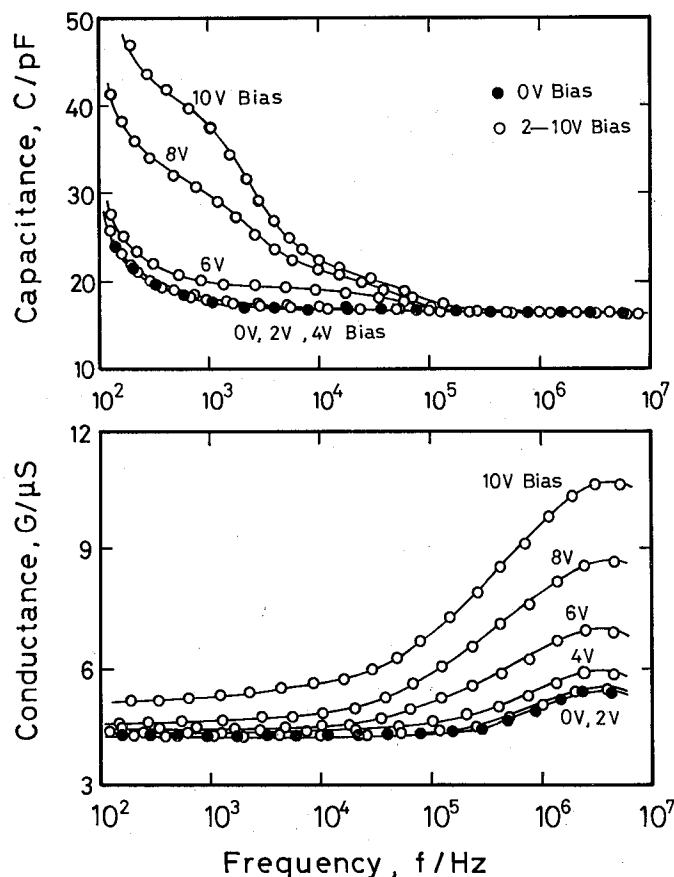


Fig. 6. Frequency dependence of capacitance C and conductance G for the whole system composed of a Sartorius membranfilter and distilled water under application of d.c. bias voltages (0V to 10V).

the Visking dialysis membrane.

On application of bias voltages of more than 4V, the increase in capacitances assigned to P-relaxations was observed around 10^3 - 10^4 Hz. The increase in conductances around 10^4 - 10^6 Hz is assigned to Q-relaxations, though the concomitant increase in capacitances is too small to be observed.

3.2. Dielectric Behaviour of Disperse Systems in Spherical Structure

3.2.1 Oil-in-Water Emulsion

A considerable number of studies for W/O emulsions and O/W emulsions have been reported by Hanai et al.^{11,12}. The results obtained from the studies showed that a dielectric relaxation was observed only for W/O type emulsion theoretically as well as experimentally. No dielectric relaxation was observed for O/W emulsions experimentally.

In the present study, an attempt was made to observe the dielectric behaviour of the O/W emulsion under application of d.c. bias voltage. The results of dielectric observation for the O/W emulsion are shown in Fig. 9. No dielectric relaxation was

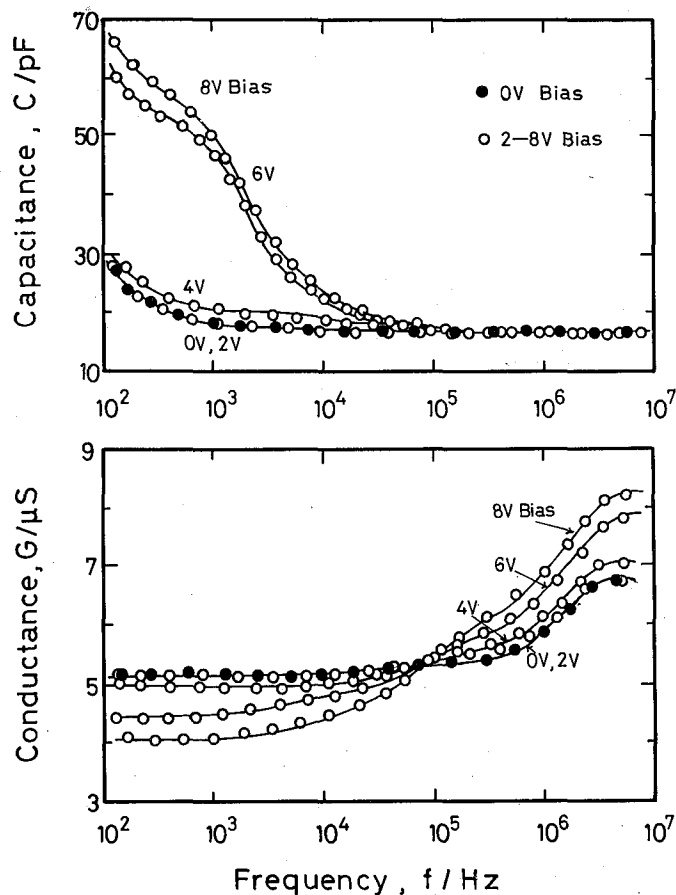


Fig. 7. Frequency dependence of capacitance C and conductance G for the whole system composed of a Nuclepore membrane and distilled water under application of d.c. bias voltages (0v to 8v).

observed for the O/W emulsion on application of d.c. bias voltage. In Fig. 9, the conductance of the O/W emulsion increases with the increase in d.c. bias voltage.

3.2.2 Polystyrene Latex

Figure 10 shows the d.c. bias effect on polystyrene latex. Remarkable dielectric relaxations were observed under application of d.c. bias voltage. The capacitances C_i at low frequencies shows a maximum value at bias voltage 4V, and then decreases with increasing bias voltage, while G_i decreases gradually with increasing d.c. bias voltage. This feature of the system is very different from other examples presented in the preceding subsections.

For a variety of examples introduced above, it is concluded experimentally that dielectric relaxation was found for most of the system under application of d.c. bias voltage. The bias effect examined for these systems are summarized in Table 1.

3.3 Analysis of Cation-Exchange Membrane

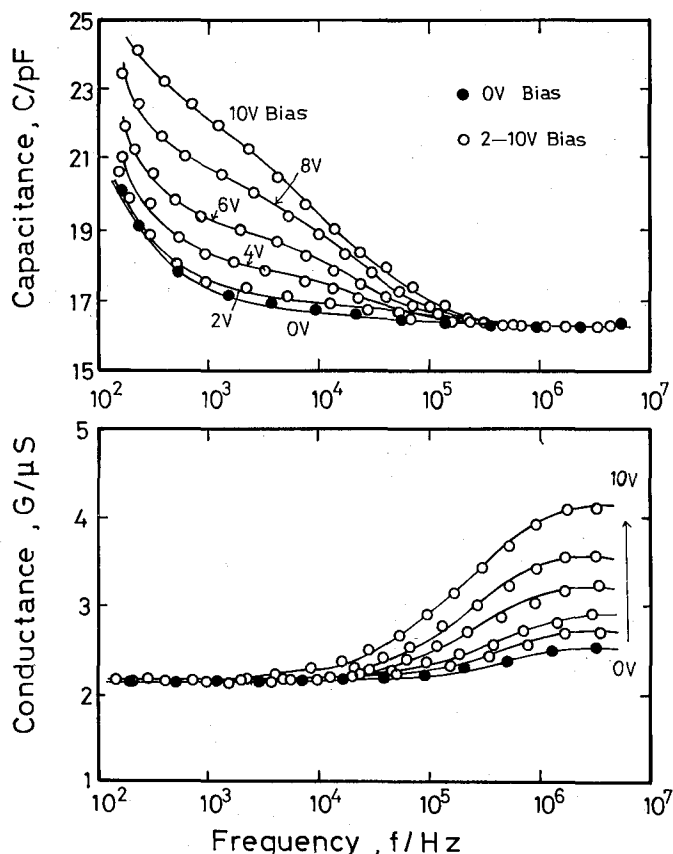


Fig. 8. Frequency dependence of capacitance C and conductance G for the whole system composed of a Milliporefilter and distilled water under application of d.c. bias voltages (0v to 10v).

A dielectric analysis for a couple of dielectric relaxations for the membrane CMV shown in Fig. 11 was formulated by Hanai et al.¹³⁾, the procedure being shown below.

The present system is assumed to consist of a thin layer p and two aqueous phases z and y with different electrolyte concentration as illustrated in Fig. 12(a). The thin layer p is a concentration polarization layer generated alongside the ion-exchange membrane on application of d.c. bias voltage. The whole system depicted in Fig. 12(a) can be represented by an equivalent circuit model shown in Fig. 12(b). Subscripts z, y and p denote the left side and the right side aqueous phase of the layer and the concentration polarization layer, respectively. The whole system of Fig. 12(b) can be represented by parallel equivalent capacitance C and parallel equivalent conductance G at each frequency as shown in Fig. 12(c).

The complex capacitance C^* of the whole system is defined in the following form:

$$C^*(f) = C(f) + \frac{1}{j2\pi f} G(f) \quad (1)$$

where f is the frequency of a.c. voltage, and j is the imaginary unit defined by $j = \sqrt{-1}$.

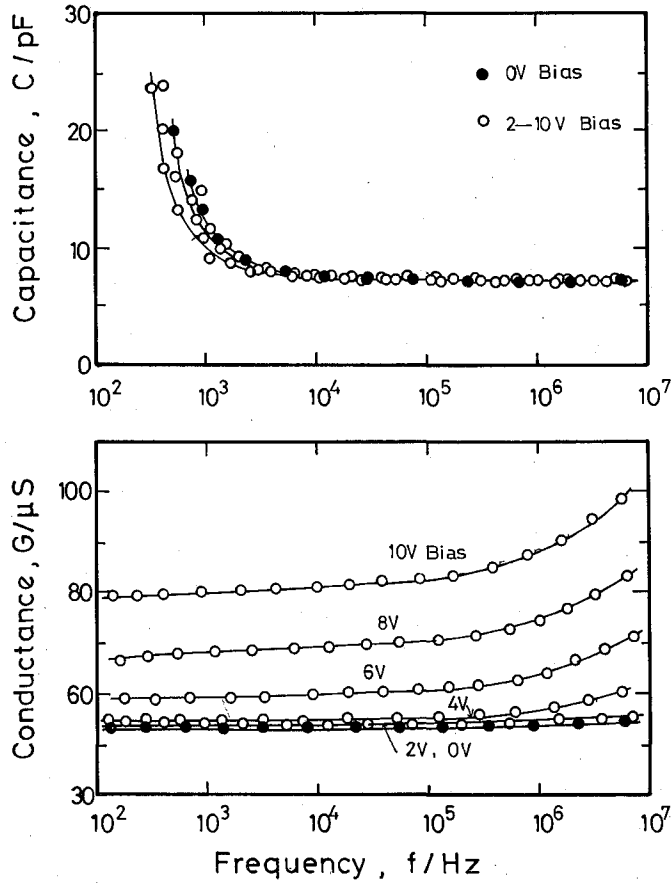


Fig. 9. Frequency dependence of capacitance C and conductance G for the O/W emulsion 50% in volume concentration under application of d.c. bias voltages (0v to 10v).

The complex capacitance C^* is also represented by the following formula:

$$\frac{1}{C^*} = \frac{1}{C_z^*} + \frac{1}{C_p^*} + \frac{1}{C_y^*}. \quad (2)$$

Here, C_p^* , C_z^* and C_y^* are complex capacitance of the concentration polarization layer p , aqueous phase z and aqueous phase y , respectively, being defined by the following formulas:

$$C_z^* = C_z + \frac{1}{j2\pi f} G_z. \quad (3)$$

$$C_y^* = C_y + \frac{1}{j2\pi f} G_y. \quad (4)$$

$$C_p^* = C_p(f) + \frac{1}{j2\pi f} G_p(f). \quad (5)$$

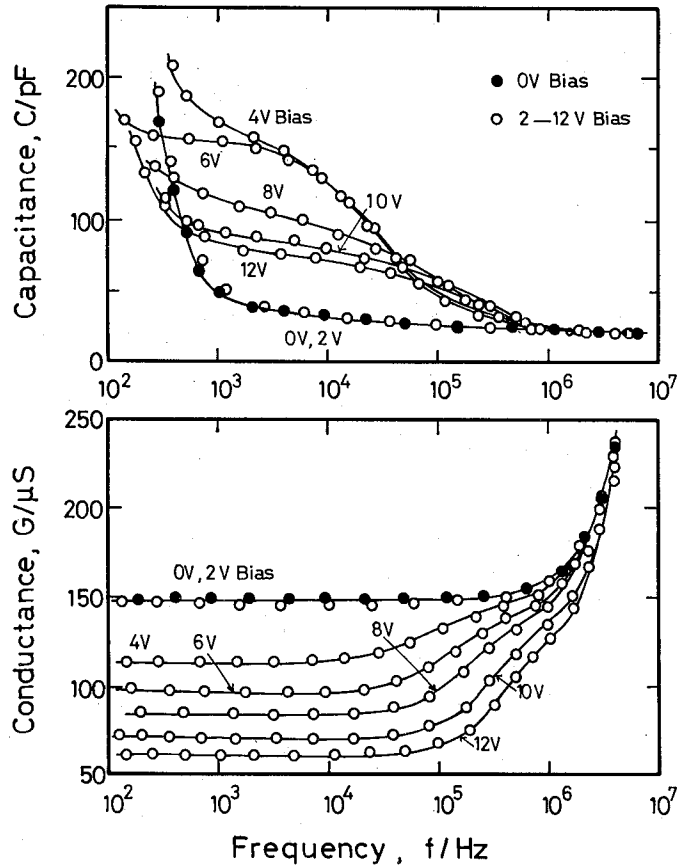


Fig. 10. Frequency dependence of capacitance C and conductance G for the polystyrene latex under application of d.c. bias voltages (0v to 12v).

$$C_p(f) = \frac{S(\kappa_\beta - \kappa_\alpha)}{2\pi f \cdot t} \cdot \frac{B}{A^2 + B^2} \quad (6)$$

$$G_p(f) = \frac{S(\kappa_\beta - \kappa_\alpha)}{t} \cdot \frac{A}{A^2 + B^2} \quad (7)$$

The structure of concentration polarization layer p is characterized by the thickness t , the conductivity κ_β at the z-phase side and the conductivity κ_α at the membrane side.

The data shown in Fig. 11 are plotted on complex planes of complex capacitance C^* and complex conductance G^* as shown in Figs. 13(a) and 13(b). In the figures, low frequency limiting value C_l , high frequency limiting value C_h , low freq. G_l and high freq. C_h can be determined with accuracy by extrapolation of the respective plots to lower and higher frequencies.

The values of dielectric parameters, C_l , C_m , C_h , G_l , G_m and G_h thus obtained are tabulated in Table 2. The capacitance C_x and C_y , conductance G_x and G_y and the conductivity κ_β and κ_α , the thickness t of the concentration polarization layer p are

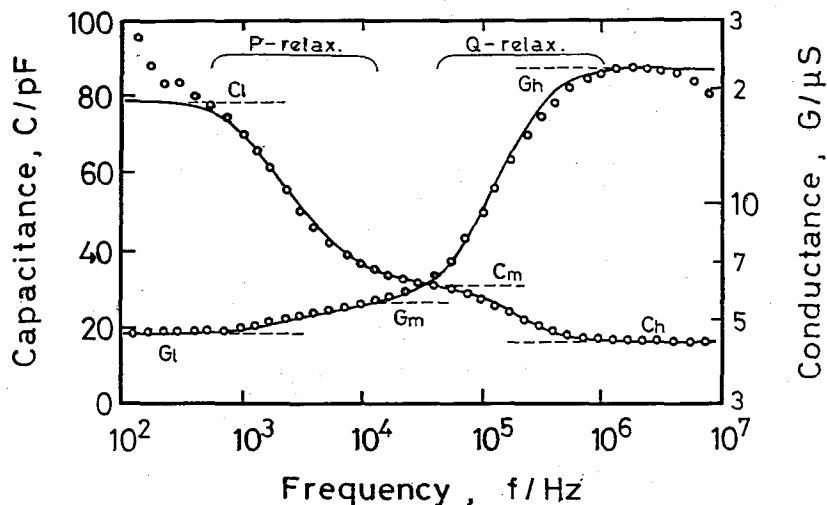
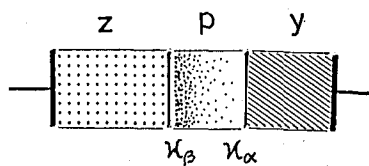
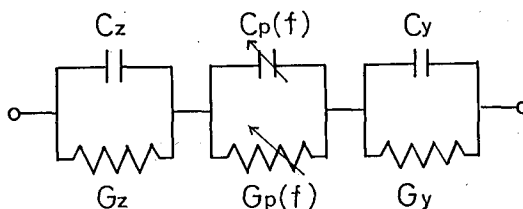


Fig. 11. Frequency dependence of capacitance C and conductance G for the whole system composed of a cation exchange membrane CMV and distilled water under a d.c. bias voltage 10V. The solid curves for C and G are calculated by means of theoretical formulae by the use of parameters obtained by the present analysis.

(a)



(b)



(c)

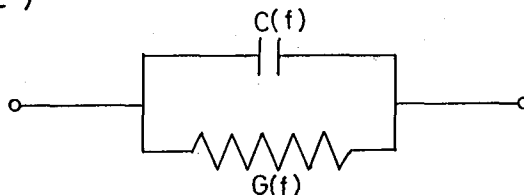


Fig. 12. (a) Diagrammatic representation of the cell system composed of a layer with locally varying conductivity and two aqueous phases being located in both sides of the film. (b) Circuit model of the cell system shown in Fig. 13(a). (c) Parallel equivalent circuit model composed of C and G .

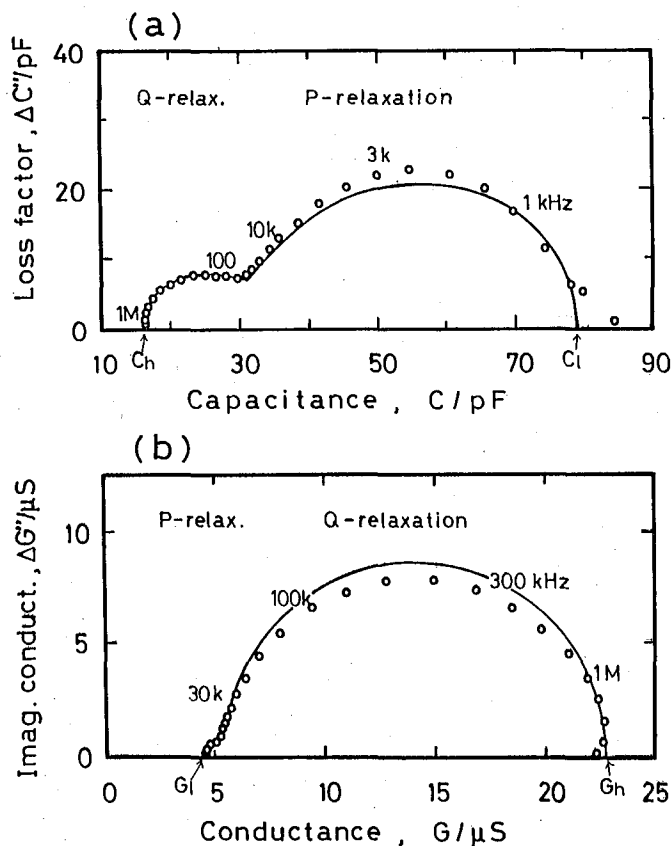


Fig. 13. (a) Complex capacitance C^* -plane plots [$C, \Delta C'' = (G - G_i)/(2\pi f)$], and (b) complex conductance G^* -plane plots [$G, \Delta G'' = 2\pi f(C - C_0)$] of the data for the D.W./CMV/D.W. system under 10V bias application. The data referring to Fig. 11. The solid curves are calculated by means of the theoretical formulas by use of parameter values obtained.

calculated by means of the computation method¹³⁾ based on a dielectric theory on concentration polarization. The results are summarized in Table 2 for respective values of d.c. bias voltage. By use of the values C_z , G_z , C_y , G_y , κ_β , κ_α , and t , the theoretical curves for $C(f)$ and $G(f)$ are calculated by use of Eqs. (1)-(7), being shown with solid curves in Figs. 11 and 13. The theoretical curves are all in good agreement with the observed points over the whole range of frequency.

The values of Table 2 supply us information pertinent to the structure of concentration polarization layer generated alongside the cation exchange membrane CMV under d.c. bias voltage. The conductivity κ_α is nearly the same as a value $0.055 \mu\text{S}/\text{cm}$ for pure water, the thickness t is in fairly good agreement with results obtained from the procedure of d.c. voltage and current observation by a number of workers.¹⁴⁻¹⁶⁾

Through the analysis of the example, it turns out possible to study fixed-charge membrane systems by means of dielectric analysis under d.c. bias voltage. The data obtained for membranes AMV were also treated with the same procedure as used for

CMV membranes and will be reported elsewhere.

3.4 Suggested Mechanism for the Dielectric Relaxation Occuring on Application of D.C. Bias Voltage

Table 1 shows much possibility of dielectric relaxation under d.c. bias voltage in various kinds of molecular assemblies: ion-exchange membranes, Visking dialysis membrane, reverse osmosis membrane, Sartorius membranfilter, Nuclepore membrane, Milliporefilter and polystyrene latex.

In the preceding subsection 3.3, the dielectric relaxations for CMV membrane systems subjected to d.c. bias voltage are interpreted theoretically as some decrease in electrolyte concentration in the aqueous phases alongside the charged membrane. This kind of decrease in concentration is expected to be generated as far as the transport numbers of cations are different from each other between the membrane and the adjoining aqueous solution.

The concentration gradient dC/dx in the aqueous solution adjacent to the membrane is given by the following relation:

$$\frac{dC}{dx} = \frac{t_+ - T_+}{D} \cdot \frac{I}{FS} \quad (8)$$

where t_+ and T_+ are the cation transport number in the aqueous solution and in the membrane phase respectively, D the diffusion coefficient of the electrolyte in the aqueous solution, I the electric current resulting from the d.c. bias voltage applied, S the area of interfaces, and F is Faraday constant.

The decrease in electrolyte concentration induced by dC/dx leads to the higher impedance, giving rise to dielectric relaxation. Such being the case, the dielectric relaxation caused by d.c. bias voltage as pointed out in Table 1 is an evidence of inequality of ionic transport number between the membranes and the ambient aqueous solutions.

Table 1. Effect of d.c. bias voltage on some molecular assemblies

Material	No bias voltage	Application of bias voltage
CMV cation-exchange membrane	×	○
AMV anion-exchange membrane	×	○
Visking dialysis membrane	×	○
Reverse osmosis membrane	×	○
Sartorius membranfilter	×	○
Nuclepore membrane	×	○
Milliporefilter	×	○
O/W Emulsion	×	×
Polystyrene latex	×	○

× : no dielectric relaxation
○ : dielectric relaxation appears

Table 2. Dielectric parameters observed and phase parameters calculated for the cell system with cation exchange membrane CMV and distilled water under application of d.c. bias voltages

Bias (volt)	C_i (pF)	C_h (pF)	C_t (pF)	G_i (μ S)	G_m (μ S)	G_h (μ S)
4	58.88	21.15	16.00	3.313	3.868	6.062
5	74.71	23.68	16.10	3.735	4.548	8.375
6	79.78	26.18	16.07	4.008	4.920	10.92
7	81.20	27.75	16.07	4.178	5.200	13.78
8	83.33	29.22	16.08	4.333	5.375	16.92
9	84.03	30.34	16.07	4.458	5.415	20.21
10	78.89	31.16	16.07	4.521	5.495	22.60
11	79.66	31.61	16.00	4.700	5.628	27.04
13	72.92	32.76	15.90	4.430	5.618	35.84
14	71.18	33.35	16.07	4.753	5.717	39.53

Table 2-B: Phase parameters of three phases z, y and p by means of computation on the basis of a dielectric theory on concentration polarization

Bias (volt)	C_z (pF)	G_z (μ S)	C_y (pF)	G_y (μ S)	κ_β (μ Scm $^{-1}$)	κ_α (μ Scm $^{-1}$)	t (mm)
4	32.36	5.425	35.44	22.87	1.166	0.03343	0.7390
5	37.81	6.698	31.50	27.06	1.232	0.03446	0.8572
6	41.02	7.202	29.46	32.68	1.221	0.03730	0.8533
7	42.00	7.558	29.28	41.73	1.252	0.04224	0.9315
8	42.28	7.574	29.01	51.18	1.246	0.04275	0.8877
9	41.34	7.213	28.90	61.56	1.213	0.03992	0.7495
10	42.39	7.394	28.61	68.01	1.213	0.04782	0.8065
11	41.02	7.244	28.66	82.96	1.228	0.04502	0.7044
13	45.82	8.285	28.29	109.87	1.257	0.07227	1.2502
14	42.78	7.512	28.62	121.72	1.221	0.06477	0.8542

In the case of the filtration membranes listed in Table 1, some possibility is suggested with respect to the origin of dielectric relaxations. A slight amount of fixed charges is expected to exist either in a form of electrolytic dissociation of the constituent high polymer molecules or in a form of physical adsorption of electrolytic ions on the surface of the membranes. This kind of fixed charges affects the ionic mobility in the membrane phase. Consequently, a cation transport number shows different values between the aqueous phase and the membrane phase. It is, therefore, inferred from Eq. (8) that the concentration gradient dC/dx increases enough to exhibit a marked dielectric relaxation.

As regards polystyrene latex different from membranous structure, the suspended polystyrene granules adsorb something electrolytic ions on the surface. It is inferred that the surface potential field due to the adsorbed ions cause locally the change in effective transport number of other ions.

4. CONCLUSION

Dielectric behaviour was investigated of some heterogeneous systems in planar or in spherical structure under application of d.c. bias voltage. A distinct double dielectric relaxation was found for most of the systems. The results have been summarized in Table 1.

A dielectric theory newly developed was applied to a typical system composed of cation-exchange membrane CMV and distilled water, and interpreted successfully the double relaxation characteristics observed. The theoretical analysis for the double relaxations derived some structural parameters such as the thickness and the conductivity gradient of the concentration polarization layer, the capacitances and the conductances of the two adjoining aqueous phases.

Other examples exhibiting the d.c. bias voltage effect as listed in Table 1 remain to be solved for future exploration.

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